More light on the 2ν5 Raman overtone of SF6: Can a weak anisotropic spectrum be due to a strong transition anisotropy?

Titre	More light on the 2ν5 Raman overtone of SF6: Can a weak anisotropic spectrum be due to a strong transition anisotropy?
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Résumé en anglais	Long known as a fully polarized band with a near vanishing depolarization ratio [η s = 0.05, W. Holzer and R. Ouillon, Chem. Phys. Lett.24, 589 (1974)], the 2ν5 Raman overtone of SF6 has so far been considered as of having a prohibitively weak anisotropic spectrum [D. P. Shelton and L. Ulivi, J. Chem. Phys.89, 149 (1988)]. Here, we report the first anisotropic spectrum of this overtone, at room temperature and for 13 gas densities ranging between 2 and 27 amagat. This spectrum is 10 times broader and 50 times weaker than the isotropic counterpart of the overtone [D. Kremer, F. Rachet, and M. Chrysos, J. Chem. Phys.138, 174308 (2013)] and its profile much more sensitive to pressure effects than the profile of the isotropic spectrum. From our measurements an accurate value for the anisotropy matrix-element $\|\langle 000020\|\Delta\alpha\|000000\rangle\|$ was derived and this value was found to be comparable to that of the mean-polarizability $((000020),\bar{\alpha},(000000))$. Among other conclusions our study offers compelling evidence that, in Raman spectroscopy, highly polarized bands or tiny depolarization ratios are not necessarily incompatible with large polarizability anisotropy transition matrix-elements. Our findings and the way to analyze them suggest that new strategies should be developed on the basis of the complementarity inherent in independent incoherent Raman experiments that run with two different incident-beam polarizations, and on concerted efforts to ab initiocalculate accurate data for first and second polarizability derivatives. Values for these derivatives are still rarities in the literature of SF6.
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